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(54) **HIGH-PURITY HARD GOLD ALLOY AND PROCESS FOR PRODUCTION THEREOF**

(57) In the process of producing a high-purity gold alloy, (1) trace elements are added and (2) heat treatment is performed, so that the hardness is increased to a level approximately equivalent to that of 18-karat gold at relatively low working ratio, thereby eliminating the drawbacks associated with high-purity gold, that is, improving the workability, heat resistance, flaw resistance, durability, etc.

A high-purity gold alloy according to the present invention can be hardened to a level approximately equivalent to that of 18-karat gold at relatively low working ratio, and the high-purity gold alloy thus hardened is not extremely softened by heat treatment performed as a post-treatment, such as brazing or welding. Even a cast article which is not subjected to plastic working has a hardness comparable to that of a hardened article which has been subjected to plastic working.

SOLUTION HEAT TREATMENT:800℃, 1 HOUR
AGING TREATMENT:250℃, 3 HOURS
WORKING RATIO:ROLLING 96%; ROLLING PLUS DICING 99.6%
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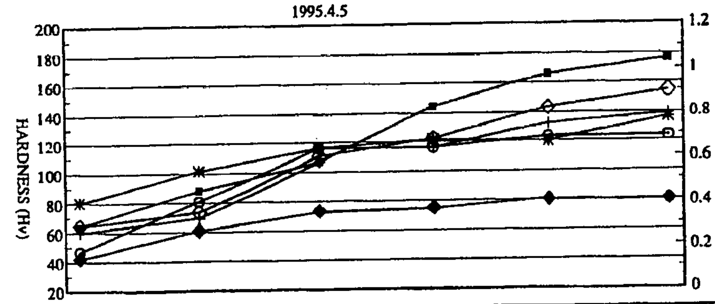

TREATMENT		CASTING	+SOLUTION HEAT -TREATMENT +AGING	+WORKING (ROLLING)	+AGING	+WORKING (DICING)	+AGING
Gd 0.138%	⊖	47	80	115	116	123	123
Gd 0.094% Ca 0.049%	■	63	88	106	145	166	176
Gd 0.110 Al 0.029	⊖	64	73	109	122	142	155
Gd 0.119 Si 0.029	✱	81	102	115	121	120	135
Ca 0.21	+	60	67	107	117	132	138
Gd 0.005	◆	43	61	73	74	80	80

FIG.1:DEPENDENCE OF HIGH-PURITY HARDENED GOLD ALLOYS OF THE PRESENT INVENTION ON HEAT TREATMENT CONDITIONS

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Description

Technical Field

Gold matrices generally used for jewelry include alloys such as 14-karat or 18-karat gold alloy, and Ni, Pd, Zn, etc. are added in large quantities to these alloys to increase their hardness or tensile strength. These alloys cannot therefore be called pure gold in respect of purity.

A high-purity gold alloy according to the present invention has a purity of 99.7% or more, and its hardness is increased to a level approximately equivalent to that of 18-karat gold at relatively low working ratio by (1) adding trace elements and (2) performing a heat treatment in the process of a production process, thereby eliminating the drawbacks accompanying the enhancement of purity, that is, improving the workability, heat resistance, flaw resistance, etc.

Background Art

High-purity gold jewelry is low in hardness and it is extremely difficult to retain its aesthetic value for a long term in daily life. Also, heat treatment performed during the production process, such as brazing, inevitably causes a great reduction in the hardness. The use of high-purity gold as ornaments is therefore limited.

Members obtained according to the present invention had a gold content of 99.85% or more and their Vickers hardness (Hv) was as high as 100 or more for cast articles and 150 or more for worked articles. Even with the use of compositions qualifying as pure gold, the hardness Hv was higher than 100 for cast articles and higher than 150 for worked articles (working ratio: 99.6%). In the case where heat treatment was performed with Gd added, the pure gold according to the present invention was remarkably increased in hardness and also improved in heat resistance. The pure gold thus obtained is less liable to be marred or scratched and undergoes less variation with time, and reduction in the hardness due to heat treatment such as brazing is small.

To obtain high-purity hardened pure gold capable of retaining high-quality look for a long term, research was conducted and as a result, a member with high hardness was obtained which contained 99.7% by weight or more of gold, to which was added 50 ppm or more of Gd as an alloying component, along with another element so that the total amount of the additional elements was 100 to 3000 ppm. Reduction in the hardness of this member due to heat treatment was small. Adding a smaller amount of the elements resulted in lower hardness, and the hardness was nearly proportional to the tensile strength.

As the heat treatment for obtaining the above high-purity gold alloy, solution heat treatment, rapid cooling and aging treatment were performed. The resulting alloy was less lowered in hardness by welding, brazing or the like and thus can retain high aesthetic value for a long term, proving to be suitable as a member for use as high-purity gold jewelry.

Disclosure of the Invention

The ornamental member according to this invention has a gold content of 99.7% by weight or more since, in general, high gold content is preferred because of high-quality look. Where 50 ppm or more of Gd was added, the hardness was increased by the heat treatment and working, and reduction in the hardness due to brazing, welding or the like lessened, showing advantageous effects of the additional element.

The addition of trace elements and the heat treatment could provide a remarkable hardening effect for both cast and worked articles. The hardened high-purity gold alloy had a gentle softening curve and was improved in hardness, tensile strength and heat resistance.

By selecting a third element to be added, it is possible to select either thermal hardening or work hardening. For cast articles, hardening is achieved by (1) adding an extra element and (2) hardening by means of heat treatment, and for worked articles, work hardening is also utilized in combination. Since the present invention employs a thermal hardening process, hardening is observed at an initial stage of the production process. The working cost could be greatly cut down and also unnecessary working time could be eliminated.

Where Gd and another element were added in combination so that these components coexisted in a total amount of 100 to 3000 ppm, the hardness was increased at an initial stage of the production process and reduction of the hardness due to application of heat could be lessened. The alloy obtained undergoes less variation with time and thus is suitable as a high-purity hardened gold alloy.

Brief Description of the Drawings

FIG. 1 shows dependence of high-purity hardened gold alloys according to the present invention on heat treatment conditions;

FIG. 2 shows dependence of high-purity hardened gold alloys on elements added;

FIG. 3 shows dependence of high-purity hardened gold alloys on aging treatment temperature; and

FIG. 4 shows dependence of high-purity hardened gold alloys on heat treatment conditions, that is, dependence on heat treatment itself.

Best Mode of Carrying out the Invention

Members according to the invention will be described with reference to specific examples. Evaluation samples shown in FIGS. 1 and 2 were obtained by

melting gold alloys having the respective compositions and pure gold by high-frequency vacuum melting, casting the melt into ingots of 20 mm × 20 mm × 150 mm, and then subjecting the ingots to heat treatment, rolling and dicing to obtain wires of 0.8 mm in diameter Φ.

In the case of evaluation samples shown in FIG. 4, wires of 8 mm in diameter Φ were obtained by continuous casting following the high-frequency vacuum melting. After the wires were subjected to solution heat treatment, aging treatment, rolling and dicing, hardness and tensile strength were evaluated and also the elements contained were analyzed.

The results reveal that the hardness can be greatly increased by performing the solution heat treatment following the casting and by performing the aging treatment following the working, thus proving high thermal hardening effect.

With regard to the gold-alloy ornamental members according to the present invention, obtained by the aforementioned process, and pure-gold ornamental members, micro-Vickers hardness (load: 100 g) was measured after the casting, before and after the heat treatment, and before and after the working. The results are shown in FIG. 1. If Gd added is small in quantity, then the effect of the heat treatment as well as the heat resistance lower. On the other hand, if an increased amount of Si is added, a crack is caused during the working. The article containing both Gd and Ca has a hardness Hv as high as 170, which is higher by about 40% than that of the article containing Gd alone and higher by about 25% than that of the article containing Ca alone.

Articles containing rare earth elements tend to show high heat resistance, and among them, the article containing Gd exhibits the highest heat resistance, proving a remarkable effect of the heat treatment as shown in FIG. 2.

The cast article containing both Gd and Si has a hardness Hv of 100, which is higher by about 64% than that of the article containing Gd alone. The article containing Si alone is extremely low in heat resistance.

For the purpose of evaluation, samples were prepared using Gd (rare earth element) showing a high age hardening effect and Ca (alkaline earth metal) showing a high work hardening effect, and excellent results were obtained in both cases. By applying the production process of the present invention using the heat treatment, it is possible to increase the hardness by approximately 30%. Similar results were obtained also in cases where elements were added in combination.

The high-purity gold-alloy ornamental member according to the present invention has high hardness and improved heat resistance, as compared with pure-gold ornamental members on the market, and the hardness thereof scarcely lowers due to application of heat. Further, the inspection after a lapse of 10 months revealed no substantial variation with the passage of time in respect of hardness, tensile strength and color tone.

Thus, the high-purity hardened gold alloy member according to the present invention can retain these properties for a long term, and accordingly, is highly useful in the industrial field where it is put to practical use in a variety of ornamental articles.

Also, the high-purity hardened gold alloy according to the present invention may probably be used in other fields, such as in electronic parts, medical parts, etc.

Claims

1. A high-Au-purity hard alloy ornamental member, characterized in that 50 ppm or more of Gd and one or more of other elements are added in combination to Au having a purity of 99.7% by weight or more such that a total content of the elements added is 100 to 3000 ppm.

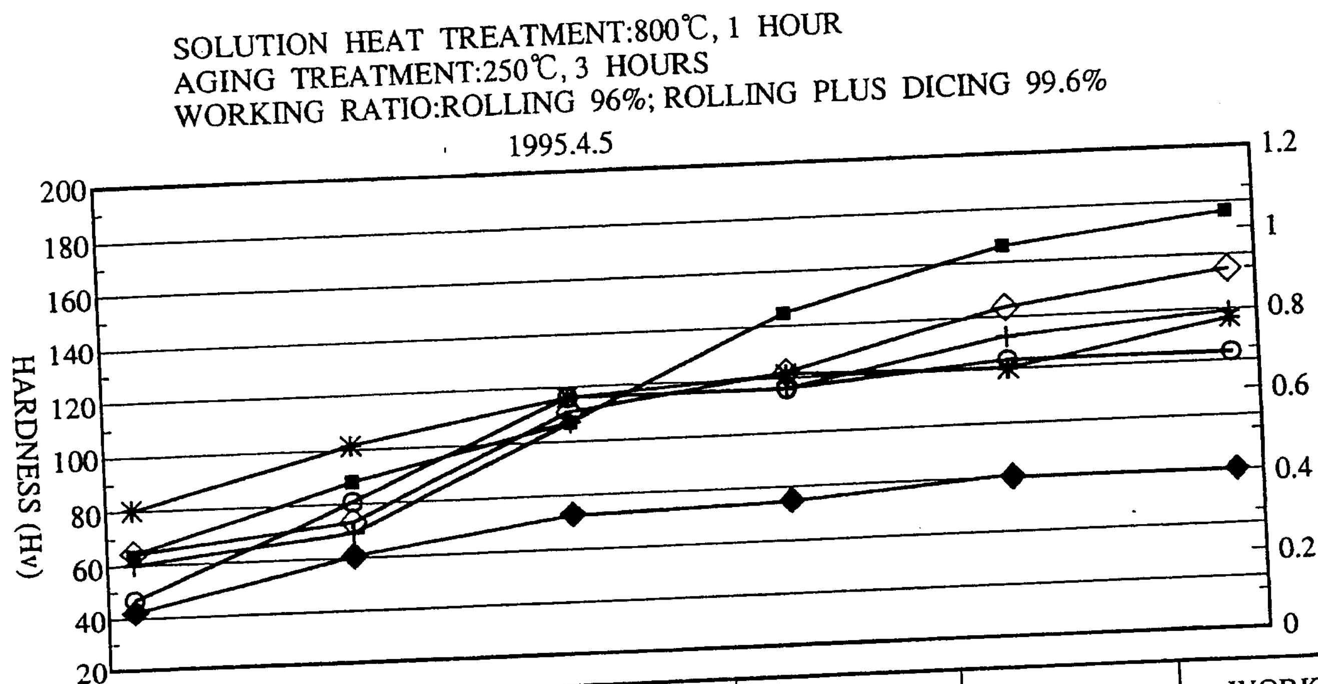
2. A high-Au-purity hard alloy member, characterized in that a combination of elements including Gd and Ca or Gd and Al (Gd: 10% or more) is added in an amount of 100 to 3000 ppm to said alloy member.

3. A high-Au-purity hard alloy member, characterized in that a combination of elements including Gd and Si (Gd: 50% or more) is added in an amount of 100 to 3000 ppm to said alloy member.

4. A process of producing a high-Au-purity hard alloy member, characterized in that, in process of producing a high-Au-purity alloy member having a purity of 99.7% by weight or more, (1) a solution heat treatment is performed at 700°C or more after casting and then an aging treatment is performed at 150 to 350°C as a post-treatment, or (2) said aging treatment alone is performed.

5. A process of producing a high-Au-purity hard alloy member, characterized in that 50 ppm or more of Gd is added to Au having a purity of 99.7% by weight or more, a solution heat treatment is performed at 700°C or more after casting and then an aging treatment is performed at 150 to 350°C as a post-treatment, or said aging treatment alone is performed.

6. A production process, characterized in that 100 ppm or more of a combination of metals selected from one or both of rare earth elements and alkaline earth metals is added to a high-Au-purity alloy member having a purity of 99.7% by weight or more, and said solution heat treatment or said aging treatment is performed.



TREATMENT	CASTING	+SOLUTION HEAT -TREATMENT +AGING	+WORKING (ROLLING)	+AGING	+WORKING (DICING)	+AGING
Gd 0.138% ⊖	47	80	115	116	123	123
Gd 0.094% Ca 0.049% ■	63	88	106	145	166	176
Gd 0.110 Al 0.029 ◇	64	73	109	122	142	155
Gd 0.119 Si 0.029 ✳	81	102	115	121	120	135
Ca 0.21 +	60	67	107	117	132	138
Gd 0.005 ◆	43	61	73	74	80	80

FIG.1:DEPENDENCE OF HIGH-PURITY HARDENED GOLD ALLOYS OF THE PRESENT INVENTION ON HEAT TREATMENT CONDITIONS

SOLUTION HEAT TREAMENT:800℃, 1 HOUR
HEAT TREATMENT:250℃, 3 HOUR

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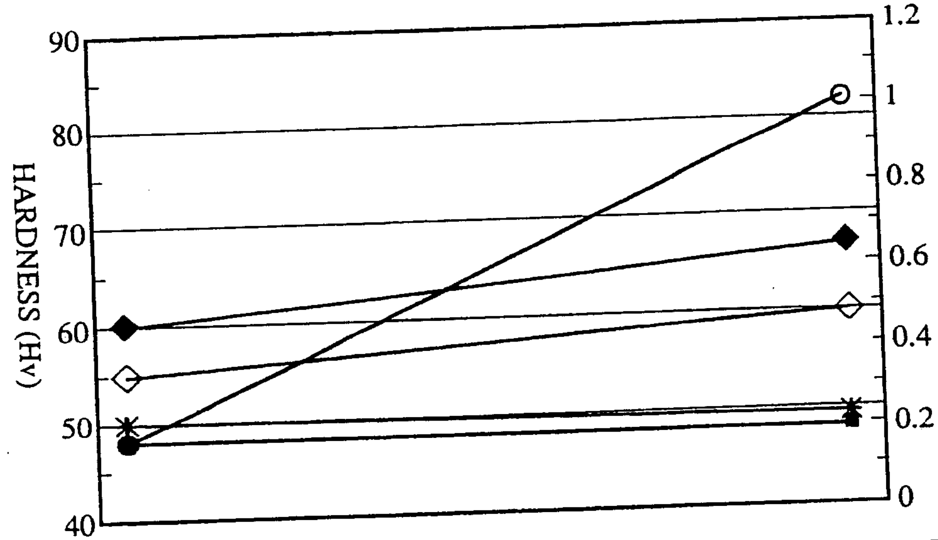

TREATMENT		CASTING	SOLUTION HEAT TREATMENT +HEAT TREATMENT
Gd 0.148%	⊖	48	82
Sm 0.160%	■	48	48
Ce 0.180%	◇	55	60
Dy 0.180	✳	50	49
Ca 0.123	◆	60	67

FIG.2:DEPENDENCE OF HIGH-PURITY HARDENED GOLD ALLOYS ON ELEMENTS ADDED

SOLUTION HEAT TREATMENT:800℃, 1 HOUR
AGING TREATMENT:250℃, 3 HOURS
WORKING RATIO:ROLLING 96% PLUS DICING 99.6% (IN TOTAL)

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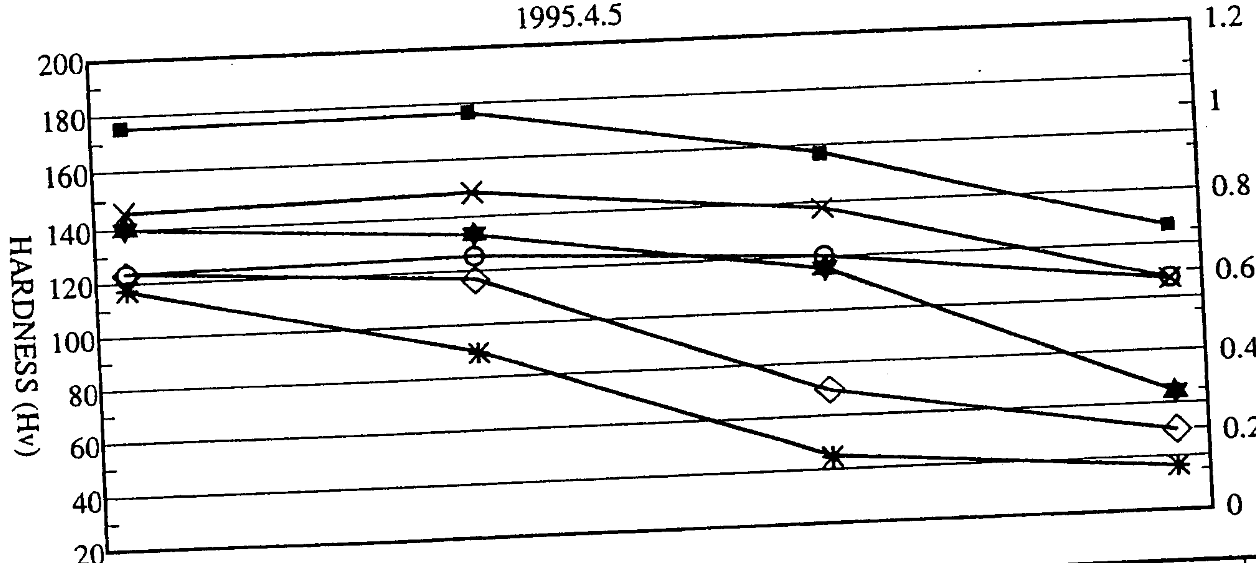
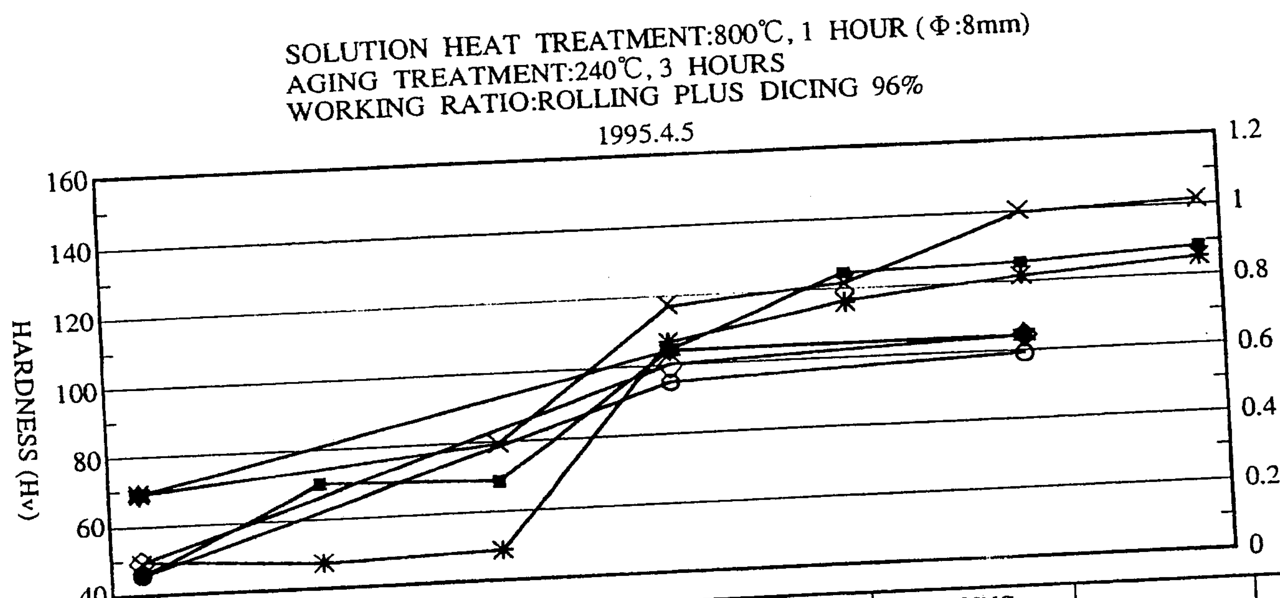


TREATING TEMPERATURE (℃)	150	250	350	450
Gd 0.149% ⊖	123	125	120	108
Gd 0.094 Ca 0.049 ■	176	177	157	126
Al 0.186 ◇	123	116	69	49
Gd 0.110 Al 0.029 ✕	146	149	137	108
Si 0.182 ✳	118	89	46	35
Gd 0.116 Si 0.031 ✱	140	133	115	65

FIG.3:DEPENDENCE OF HIGH-PURITY HARDENED GOLD ALLOYS OF THE PRESENT INVENTION ON AGING TREATMENT TEMPERATURE



TREATMENT	CASTING	SOLUTION HEAT -TREATMENT (800℃, 1 HOUR)	AGING TREATMENT (250℃, 3 HOURS)	ROLLING 90%	AGING TREATMENT (250℃, 3 HOURS)	DICING T99%	AGING TREATMENT (250℃, 3 HOURS)
Gd 0.139% NOT HEAT TREATED ⊖	46			95		99	
HEAT TREATED ■	46	70	68	104	125	126	128
Sm 0.159 NOT HEAT TREATED ◇	49			100		104	
NOT HEAT TREATED ✳	49	47	48	106	115	122	125
Gd 0.072 Sm 0.092 NOT HEAT TREATED ✸	69			104		104	
HEAT TREATED ×	69		79	117	122	140	142

FIG.4:DEPENDENCE OF HIGH-PURITY HARDENED GOLD ALLOYS OF THE PRESENT INVENTION ON HEAT TREATMENT CONDITIONS DEPENDENCE ON HEAT TREATMENT

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP96/00510

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl^6 C22C5/02, C22F1/14

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int. Cl^6 C22C5/02, C22F1/14

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho	1926 - 1996
Kokai Jitsuyo Shinan Koho	1971 - 1996
Toroku Jitsuyo Shinan Koho	1994 - 1996

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	JP, 7-70670, A (Mitsubishi Materials Corp.), March 14, 1995 (14. 03. 95), Column 1, lines 2 to 21, 42 to column 2, line 34; tables 1 to 4 (Family: none)	1 - 3 4 - 6
Y	JP, 7-70671, A (Mitsubishi Materials Corp.), March 14, 1995 (14. 03. 95), Column 1, lines 23 to 32 (Family: none)	2, 4-6
X Y	JP, 7-90425, A (Tanaka Kikinzoku Kogyo K.K.), April 4, 1995 (04. 04. 95), Column 1, lines 2 to 11, 40 to column 2, line 3 (Family: none)	1 2 - 6
Y	JP, 63-57753, A (Citizen Watch Co., Ltd.), March 12, 1988 (12. 03. 88), Page 1, lower left column, lines 5 to 14; page 2, upper left column, lines 14 to 18 (Family: none)	4 - 6

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document but published on or after the international filing date
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"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search August 5, 1996 (05. 08. 96)	Date of mailing of the international search report August 13, 1996 (13. 08. 96)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.